Isothermal Adsorption Model of Reduction of Ni^{2+} Ion by Chitosan Membrane of Rice Snail Shell (Pilla ampullaceal)

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Abstract. Heavy metals are detrimental to living organisms and ecosystems because they are non-biodegradable and accumulate in the environment and food chain. The research objective was to determine the maximum contact time, pH, and the isothermal adsorption model for the adsorption of Ni^{2+} ions by the chitosan membrane of rice snail shells. Contact time and pH are determined by varying these variables. The Langmuir and Freundlich isothermal model was analyzed by varying the initial ion Ni^{2+} concentrations The results showed that the adsorption of Ni^{2+} ion has 120 min of maximum contact time with 72,52% Ni^{2+} ions that could be adsorbed, while the optimum pH at pH 5 with Ni^{2+} ions adsorbed by 60.96% . The isothermal adsorption model of rice snail shell chitosan membrane adsorbs ions Ni^{2+} following the Freundlich isothermal model with the equation y = 0.9172 x – 0.3698 and R2 = 0.9203 and the capacity adsorption was 2.343 g/L.

Keywords: Isothermal Adsorption · Chitosan Membrane · Ni^{2+} ion · Contact time · pH

1 Introduction

Industrial growth will affect environmental conditions. Liquid waste containing heavy metals causes significant threats to the environment and public health. Heavy metals are toxic, nonbiodegradable, persistent, and bioaccumulation in the food chain and can enter humans through the food chain [1–4]. One of the heavy metals is nickel. Nickel is toxic and enters the human body in several ways: inhalation, oral, and derma. Nickel has adverse health effects and is toxic to vital organs such as the lungs, kidneys, and others causing illness or health problems, In addition, some nickel compounds are carcinogenic, causing cancer and even death [4–6]. Therefore, the presence of the metal needs to be minimized or even eliminated. One of the methods is using the adsorption method by utilizing natural polymers as adsorbents, such as chitosan [7–9].

Chitosan is produced from the deacetylation process of chitin and is composed of glucosamine and N-acetylglucosamine [10–12]. Metal ions are bonded to amino groups and hydroxyl groups in the molecule [13]. Chitosan is a non-toxic compound, with biodegradability, biocompatibility, effectiveness at low ion concentrations, selectivity,

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and high adsorption capacity [14, 15]. Modification of chitosan to be a membrane was carried out to increase its adsorption capacity.

The membrane is semipermeable, hydrophilic, non-toxic, biodegradable, large surface area, and can be reused [16]. The membrane functions as a thin selective barrier between the two phases by only passing through the membrane certain components. However, the membrane has a weakness that is resistant to acids and brittle, so a cross-linking agent is used to stabilize the chitosan membrane [17, 18]. The adsorption process is influenced by pH and contact time. The best pH to adsorb Ni^{2+} ions by tripolyphosphate-modified chitosan was pH 5 [19]. Contact time. 60 min, temperature 35 °C, and pH 7 and obtained an adsorption efficiency of 75, 17% [20]. The practical or dynamic adsorption capacity of chitosan membrane is explained by the adsorption isotherm model. The research aimed to analyze the contact time and pH and determine the isothermal equilibrium model adsorption of the metal ion Ni^{2+} by chitosan membrane.

2 Material and Methods

2.1 The Material

The materials consisted of rice snail shell chitosan, glutaraldehyde, and $NiCl_2$. The analytical grade was used for reagents and solvents.

2.2 Experimental Procedure

The Fabrication of Chitosan Membrane. The rice snail shell chitosan used has a degree of deacetylation of 80.7% [21]. The procedure of chitosan membranes is based on [18] with several modifications. Chitosan powder as much as 3 g of paddy snail shells was stirred until homogeneous in 250 ml of 1% acetic acid. Furthermore, the mixture was a stand-in for 6 h to remove air bubbles. Then it was poured into glass dishes and dried. The chitosan membrane was immersed in 1% NaOH solution, washed with aquadest several times until neutral pH, and dried. Next, the Chitosan membrane was dipped into 50 mL of 0.4% glutaraldehyde solution containing 5 mL of 0.5 N H_2SO_4, then washed repeatedly and dried.

Determination of Optimum Contact Time of Chitosan Membrane Against Ni^{2+} Ion. A total of 30 mL of 100 ppm Ni^{2+} was added to a beaker glass that contained a chitosan membrane. Then allowed to stand-in contact for 30, 50, 70, and 90 min. Then the obtained filtrate was analyzed by Atomic Absorption Spectroscopy (AAS).

Determination of pH of Ni^{2+} Adsorption by Chitosan Membrane. A total of 30 mL samples of 100 ppm Ni^{2+} solution were adjusted to pH from 4, 5, 6, and 7 by adding a buffer solution. Each solution was put into a beaker containing a chitosan membrane. Adsorption is carried out with the optimum contact time that has been obtained. Then the obtained filtrate was analyzed by Atomic Absorption Spectroscopy (AAS).

Percentage adsorption:

$$\%\ \text{absorption} = \frac{\text{Co} - \text{Ce}}{\text{Co}} \times 100\% \tag{1}$$

Description: % = percentage
Co = Initial concentration
Ce = concentration adsorbate in equilibrium

Determination of Isothermal Adsorption of Chitosan Membrane. The isothermal adsorption of the chitosan membrane was analyzed by the isotherm adsorption model. Determination is done by making various concentrations of Ni^{2+}, namely 10, 20, 30, 40, 50, 75, 100, 125, and 150 ppm, and later adsorption was carried out on the chitosan membrane by adjusting adsorption conditions at the best pH and contact time. Next, they were filtered and the filtrate obtained was measured for absorbance using AAS. The Ni^{2+} adsorption model is determined by the Langmuir and Freundlich isotherm.

Isothermal Langmuir equation:

$$\frac{Ce}{Qe} = \frac{Ce}{Qm} + \frac{1}{KlQm} \tag{2}$$

Isothermal Freundlich equation:

$$\text{In } Qe = \text{In } Kf + \frac{1}{n}\text{In } Ce \tag{3}$$

Description: kf is the Freundlich constant or capacity adsorption
Ce is the concentration of adsorbate I equilibrium (mg/L).
n is the non-linear degree,
Qm is the adsorption capacity of Langmuir
Kl is Langmuir constant.

3 Results and Discussion

3.1 Contact Time Determining of Ni^{2+} Ion Adsorption by Chitosan Membranes

The contact time determines the time need the adsorbent to adsorb Ni^{2+} ions. This research was conducted with a variation of the contact time of 30–120 min as shown in Fig. 1.

Figure 1 shows that the adsorbed Ni^{2+} ions increased with increasing contact time up to 120 min. The increase in adsorption indicates an adsorption process by the chitosan membrane adsorbent. The contact time affects the ability chitosan membrane to bind Ni^{2+} ion. The longer the Ni^{2+} ion and chitosan membrane contact, the more bonding occurs between them until it reaches the maximum adsorbent condition. This is because the longer the contact time between the adsorbent and the adsorbate, the more bonds are formed between them. From Graph 1, it can be seen that the adsorption contact time continues to increase significantly. Based on the graph, the 120-min is chosen as the best time for the adsorption of Ni^{2+} ions by the chitosan membrane. At this time, the equilibrium condition has not been reached because it is estimated that the adsorption of Ni^{2+} metal ions is still occurring.

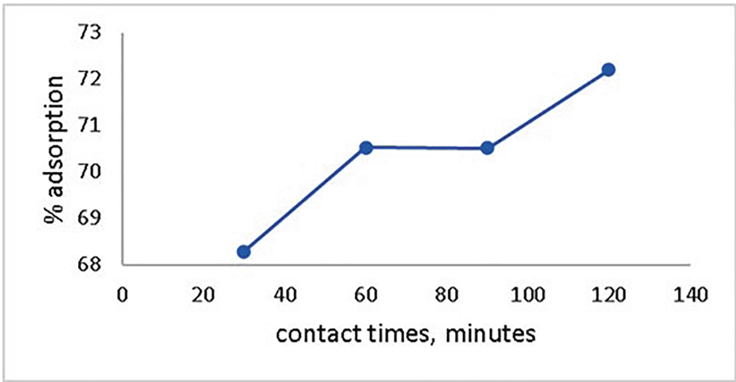

Fig. 1. The contact time of Ni^{2+} ion adsorption by chitosan membrane

3.2 Determination of pH in Ni^{2+} Ion Adsorption by Chitosan Membrane

The metal ion adsorption process is strongly influenced by pH conditions. In this study, the amount of Ni^{2+} ions adsorbed by the chitosan membrane was determined by varying the pH 4–7 with a contact time of 120 min (maximum contact time) as shown in Fig. 2.

Based on Fig. 2, at pH 4 the amount of adsorbed Ni^{2+} ions is small and continues to increase until pH 7. However, at pH 6–7, there is a slight increase in ions adsorb so the adsorption process is estimated to reach equilibrium. Increasing the pH did not increase the adsorption rate significantly. At acidic pH, competition occurs between H^+ ions and Ni^{2+} ions to bind to the adsorbent functional groups. The active group of chitosan, namely NH_2, is protonated to $NH_3{}^+$. The abundance of H^+ ions causes competition with Ni^{2+} ions in interacting with the amine groups on the chitosan membrane.

Adsorption increased when the pH of the solution was 5 with an increase in % adsorption of 4.5%. This is because as the pH increases, the number of H^+ ions in

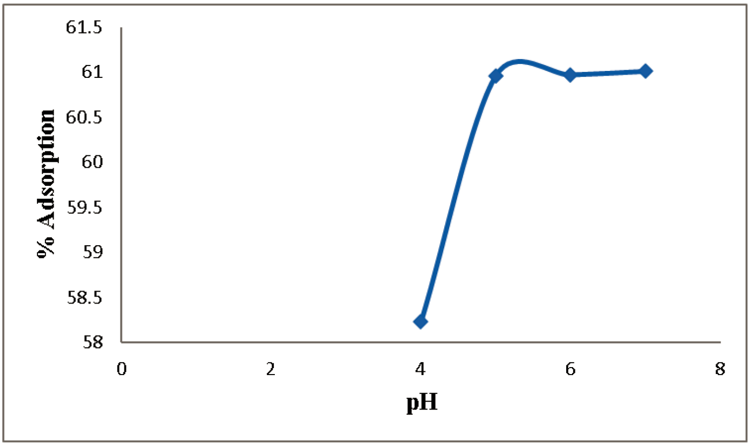

Fig. 2. pH Vs % adsorption of Ni^{2-} by chitosan membrane

solution decreases which causes fewer amine groups to be protonated. Furthermore, at pH 6–7, adsorption tends to be spontaneous the higher the pH conditions, the more OH^- ions in the solution so that the Ni^{2+} ions become $Ni(OH)_2$ which will precipitate. In addition, the concentration of H^+ ions decreases which results in the active group of chitosan being in the form of NH_2 and can react with Ni^{2+} ions to form the NH_2Ni_2 complex. Based on research, pH 5 is the optimum pH in the adsorption of Ni^{2+} ions by the chitosan membrane.

3.3 Ni^{2+} Ion Adsorption Isothermal by Chitosan Membrane

Determination of the isothermal adsorption of Ni^{2+} ions by chitosan membrane using Langmuir and Freundlich adsorption isothermal equations. The Langmuir model states that the adsorption process occurs in a monolayer [22]. Freundlich explained that adsorption occurs on the surface of the adsorbent which is heterogeneous (multilayer). The equations of Langmuir was in Fig. 3.

Based on Fig. 3, the Langmuir equation was $y = 0.2416\ x + 3.2389$, and R^2 was 0.2875. Indicated, a big error. The equation becomes $(Ce)/Qe = 0{,}041Ce + 3$, the value of adsorption capacity was 24.038 mg/gr, and the value of b or K was maximum.

The Freundlich model states that the adsorption is in a multi-layer means a solid surface absorbs one layer of adsorbate molecules, then the solid form a new adsorption layer and adsorbs another adsorbate [22]. The Freundlich isothermal model can be seen in Fig. 4.

Based on Fig. 4, the equation of the Freundlich isothermal model was $y = 0{,}8172\ x - 0{,}3690$ with R^2 being 0,9203. The value of R^2 is close to 1 so the adsorption process of Ni^{2+} ions by the chitosan membrane follows the Freundlich adsorption isothermal equation. The Freundlich approach assumes that the adsorbent surface is heterogeneous and the adsorption forms many layers. The adsorption process takes place in physisorption where the adsorbate is not tightly bound to the adsorbent so that the adsorbate can move freely on the surface of the adsorbent. Ni^{2+} ions move freely on the surface of the

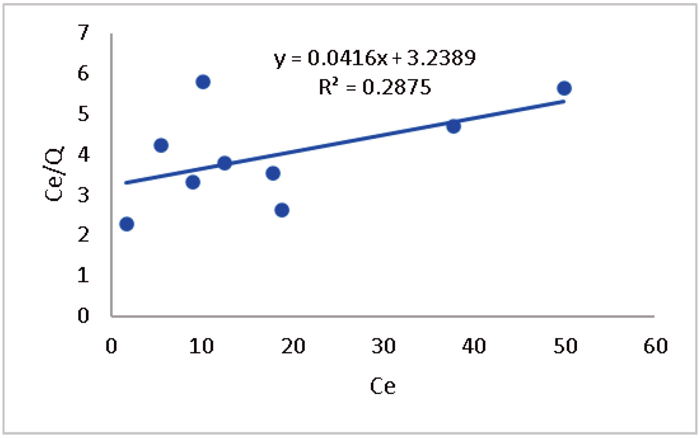

Fig. 3. Langmuir isothermal model of Ni^{2+} ion adsorption

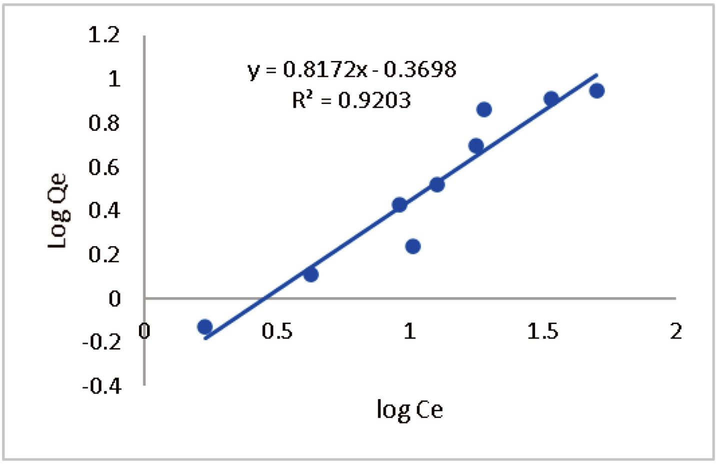

Fig. 4. Freundlinch isothermal of Ni^{2+} ion adsorption

adsorbent. The bond formed between Ni^{2+} ions and the surface of the adsorbent is a Van der Waals bond so that Ni^{2+} ions are not tightly bound to the surface of the adsorbent. This process usually occurs in a fast reversible process, so it is easily replaced with other molecules. As is shown the value of $1/n = 0.8172$ confirms that the absorption process is on a heterogeneous surface [23, 24]. The value of n obtained in this work is greater than 1, informing the physical process support in adsorption [1]. The kf value or adsorption capacity of 2.343 g/L.

4 Conclusion

The maximum contact time to adsorb Ni^{2+} ions by a chitosan membrane were 120 min and pH 5. The Ni^{2+} ions by chitosan membrane followed Freundlich's isothermal model with an R^2 was 0.9203 which is close to 1 and an adsorption capacity of 2.343 g/L. While the value an R^2 of Langmuir was 0.233.

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